fresh solvent to remove any ethylene that might have been formed in the reaction of triethyloxonium fluoroborate with sodium cobalt tetracarbonyl. This solution gave the same analysis as the solution which had not been evaporated.

In a series of similar experiments carried out with a heated inlet at only 170° about 0.14% ethylene was found (about 50% of theor.).

When the same reaction was carried out in the presence of CO and, therefore, formed the propionylcobalt tetracarbonyl, pyrolysis at 170° yielded the same amounts of products as the reaction run under nitrogen at 170°.

Effect of CO upon the Addition of Cobalt Hydrotetracarbonyl to 1-Pentene.—Two experiments were carried out in the same manner except that one was done under CO and the other under nitrogen. In the gasometric apparatus, which had been filled and flushed with the pentane-saturated gas at 0°, was placed 15 ml. of 1-pentene. To this was added 2.0 ml. of 0.46 M cobalt hydrotetracarbonyl in n-pentane. After 15 minutes, 0.5 ml. of dicyclohexylethylamine was added and the infrared spectrum was taken on a Beckman IR-7 infrared spectrophotometer. The reaction carried out under CO absorbed about 5 ml. of gas.

Mechanisms of Elimination Reactions. XXIII. Phenyllithium-induced Dehydrochlorination of the Isomeric Chlorodiphenylethenes[1]

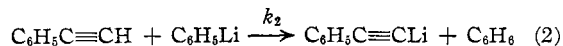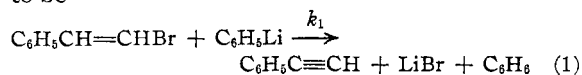By Stanley J. Cristol and Robert S. Bly, Jr.
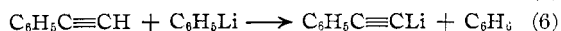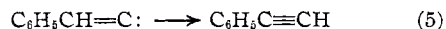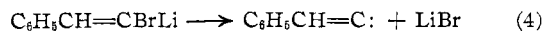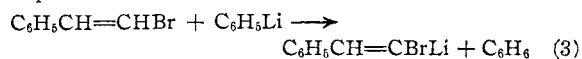
The rates of phenyllithium-induced dehydrochlorination of 2-chloro-1,1-diphenylethene and cis- and trans-1-chloro-1,2-diphenylethene have been measured in n-butyl ether. The reactions are shown to be first order in chloroethene and first order in base; the product in each case is tolan. Under the conditions employed in this study, α-elimination proceeds more readily than cis-β-elimination, which is in turn more facile than trans-β-elimination. Possible mechanisms for these reactions are considered.

Introduction

In an earlier paper in this series,[2a] it was reported that the reaction of excess phenyllithium in n-butyl ether with both cis- and trans-1-bromo-2-phenylethene gives phenylacetylene in each case, is kinetically first order in phenyllithium and first order in 1-bromo-2-phenylethene and that at 2.10°, cis elimination is preferred to trans elimination by a factor of 5.5. The course of the reaction appears to be

$$C_6H_5CH{=}CHBr + C_6H_5Li \xrightarrow{k_1}$$
$$C_6H_5C{\equiv}CH + LiBr + C_6H_6 \quad (1)$$

$$C_6H_5C{\equiv}CH + C_6H_5Li \xrightarrow{k_2} C_6H_5C{\equiv}CLi + C_6H_6 \quad (2)$$

where $k_2 \gg k_1$. When competitive experiments were performed in ethyl ether at 25°, cis elimination was preferred over trans by a factor of 2. An α elimination mechanism was postulated to explain these results.

$$C_6H_5CH{=}CHBr + C_6H_5Li \longrightarrow$$
$$C_6H_5CH{=}CBrLi + C_6H_6 \quad (3)$$

$$C_6H_5CH{=}CBrLi \longrightarrow C_6H_5CH{=}C{:} + LiBr \quad (4)$$

$$C_6H_5CH{=}C{:} \longrightarrow C_6H_5C{\equiv}CH \quad (5)$$

$$C_6H_5C{\equiv}CH + C_6H_5Li \longrightarrow C_6H_5C{\equiv}CLi + C_6H_6 \quad (6)$$

It was pointed out that 3 and 4 might be combined and/or 5 and 6 replaced by 7

$$C_6H_5CH{=}C{:} + C_6H_5Li \longrightarrow C_6H_5C{\equiv}CLi + C_6H_6 \quad (7)$$

In support of this mechanism, the relative inertness of 2-bromo-3-phenyl-2-propene, in which the α-hydrogen[3] is replaced by a methyl group,[4a] was

pointed out, as was the known propensity for strong bases such as the organolithiums and the alkali amides to initiate α-elimination reactions.[2a] The discrepancy between the reported third-order kinetics for the reaction of 1-chloro-2-phenylethene with phenyllithium[4] and the demonstrated second-order kinetics for reactions 1 and 2[2] has not yet been clarified.

In order to understand better the relative steric and energetic requirements of α- and β-eliminations, we decided to examine in some detail the phenyllithium-initiated dehydrohalogenation of 1-chloro-cis-1,2-diphenylethene (I), 1-chloro-trans-1,2-diphenylethene (II) and 2-chloro-1,1-diphenylethene (III).[5]

These three isomeric chlorodiphenylethenes can be easily prepared and distinguished; each can lose the elements of hydrogen chloride in a unique manner; i.e.

$$\begin{array}{c} C_6H_5 \qquad C_6H_5 \\ \diagdown \qquad \diagup \\ C{=}C \qquad \xrightarrow{cis\text{-}\beta} IV \qquad (8) \\ \diagup \qquad \diagdown \\ H \qquad Cl \\ I \end{array}$$

$$\begin{array}{c} C_6H_5 \qquad Cl \\ \diagdown \qquad \diagup \\ C{=}C \qquad \xrightarrow{trans\text{-}\beta} C_6H_5C{\equiv}CC_6H_5 \qquad (9) \\ \diagup \qquad \diagdown \\ H \qquad C_6H_5 \\ II \qquad\qquad IV \end{array}$$

$$\begin{array}{c} C_6H_5 \qquad Cl \\ \diagdown \qquad \diagup \\ C{=}C \qquad \xrightarrow{\alpha} IV \qquad (10) \\ \diagup \qquad \diagdown \\ C_6H_5 \qquad H \\ III \end{array}$$

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(1) (a) This work was presented in part at the 14th National Organic Symposium at Lafayette, Ind., in June, 1955. (b) Previous paper in this series: S. J. Cristol and F. R. Stermitz, *J. Am. Chem. Soc.*, **82**, 4692 (1960).
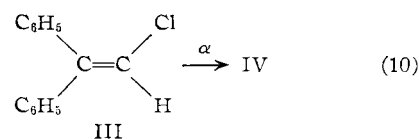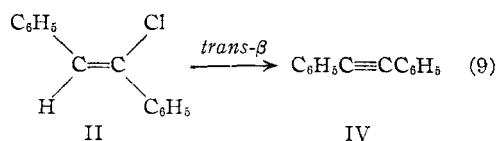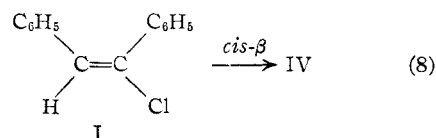
(2) (a) S. J. Cristol and R. F. Helmreich, *ibid.*, **77**, 5034 (1955); (b) R. F. Helmreich, Ph.D. Thesis, Department of Chemistry, University of Colorado, 1953.

(3) The carbon to which the departing halogen is attached will be referred to as the "α carbon" throughout this paper. The expression "β carbon" will be used to designate the adjacent carbon that participates in the formation of the double or triple bond.

(4) (a) G. Wittig and G. Harborth, *Ber.*, **77B**, 315 (1944); (b) G. Wittig, *Angew. Chem.*, **62**, 231 (1950); (c) O. Grummitt and J. J. Lucier, Abstracts of Papers presented before the 121st Meeting of the American Chemical Society, Buffalo, N. Y., March, 1952, p. 49-K.

(5) A study of the sodium hydroxide in ethanol-initiated dehydrohalogenations of these compounds will be reported in a later paper.

which permits the unequivocal comparison of cis- and trans-β-elimination with α-elimination.

α-Eliminations in this system were first studied by Fritsch,[6] Buttenberg[7] and Wiechell.[8] Buttenberg[7] has shown that when 2-chloro-1,1-diphenylethene (III) is heated with sodium ethoxide in ethanol at 180°, the main product is ethyl 2,2-diphenylvinyl ether; tolan (IV) is formed in 9% yield. Fritsch[6] and Wiechell[8] extended this reaction to some 2-chloro-1,1-bis-(p-Z-phenyl)-ethenes. When Z was CH₃O-, C₂H₅O-, C₆H₅- or CH₃-, the corresponding p,p'-disubstituted tolan was the only product isolated; no vinyl ethers were found. When Z was methyl, for example, the yield of p,p'-dimethyltolan was 95%. Other bases also have been used. Fritsch has prepared 3,3',4,4'-tetramethoxytolan from 1,1-bis-(3,4-dimethoxyphenyl)-2-chloroethene by the use of potassium amoxide. Coleman, Maxwell and Holst[9] have shown that in some cases much better yields of the tolan can be obtained by the use of potassium amide in liquid ammonia. Thus substituted tolans have been formed in 85–90% yield from the corresponding 2-chloro-1,1-diarylethenes when the aryl groups were phenyl, o-, m- or p-tolyl, o-, m- or p-anisyl, and xenyl; but with p-ethyl, propyl or butyl substituents, an impurity is formed and the yields of the tolan are reduced to 50–70%. These investigators also showed that there was no significant variation in the yield when bromoethenes were used instead of chloroethenes, or when sodium amide was substituted for potassium amide. They found that the position of attachment of groups on the benzene ring was not changed during the migration.

Several publications have appeared since the start of our work on this problem, which shed additional light upon the rearrangement of 1,1-diaryl-2-haloethenes to the corresponding diarylacetylenes under the influence of various bases. Both Bothner-By and Prichard[10] and Curtin, Flynn and Nystrom[11] have demonstrated that cis- and trans-2-bromo-1-p-halophenyl-1-phenylethene 1-^{14}C undergo dehydrobromination and rearrangement on treatment with either t-butoxide in refluxing t-butyl alcohol[10] or n-butyllithium in ethyl ether at −35°.[11] The predominant (∼90%) p-halophenylphenylacetylene-1-^{14}C in every case is that one which would be formed by migration of the aryl group which is trans to the departing bromide. More recently, Curtin, Flynn, Nystrom and Richardson[12] have investigated the reaction of some other 1,1-diaryl-2-haloethenes with n-butyl-

lithium in ethyl ether at temperatures as high as 22°. They have found that the principal, and sometimes exclusive, product is the corresponding diarylacetylene. We will discuss the consequences of this work more fully later in this paper.

From these facts, it is clear that the elimination-rearrangement reaction of 1,1-diaryl-2-haloethenes, to give the corresponding diarylacetylene, is a general reaction which occurs under the influence of a variety of bases and reaction conditions. We know of no systematic study of the kinetics of this and of the related acetylene-forming elimination reactions of the 1,2-diaryl-1-haloethenes, prior to the initiation of the work reported in this paper.

Experimental

2,2-Dichloro-1,1-diphenylethane was prepared in 60% yield according to the method of Buttenberg.[7] Recrystallization from aqueous ethanol gave a material melting at 72–75° (lit.[7] 74°).

2-Chloro-1,1-diphenylethene was obtained by allowing 2,2-dichloro-1,1-diphenylethane to react with excess ethanolic sodium hydroxide under reflux. The yield of crude material, m.p. 36–41°, was 91%. The product was purified by distillation, b.p. 127–129° (1.0 mm.), and by recrystallization from aqueous ethanol to yield white plates, m.p. 39.5–42° (lit.[7] 42°).

1-Chloro-cis- and trans-1,2-diphenylethene were prepared by the ethanolic sodium hydroxide-induced dehydrochlorination of meso- and dl-1,2-dichloro-1,2-diphenylethanes.[18] In the case of the trans isomer, the time required for the elimination to go to 99% completion was calculated from the known rate constant,[13] and the reaction was quenched after this period of time to minimize the formation of tolan. The 1-chloro-cis-1,2-diphenylethene was purified by distillation, b.p. 97–99° (0.25 mm.), (lit.[14] 160–162°[12 mm.]), n[20]D 1.6280. The trans isomer was purified by recrystallization from aqueous ethanol; m.p. 52–54° (lit.[14] 52°).

Phenyllithium Solutions.—A mixture of 157 g. (1.00 mole) of bromobenzene and 13.9 g. (2.00 moles) of lithium ribbon was allowed to react under anhydrous conditions in ethyl ether. After the reaction was complete, the ethyl ether was removed by vacuum distillation through a 20-cm. Vigreux column, with the simultaneous addition of purified n-butyl ether. The resulting solution was filtered through a glass frit and stored in a polyethylene bottle under purified nitrogen. The preparation was carried out in an apparatus designed so that all of the operations could be accomplished in an atmosphere of purified nitrogen. The final solution was 0.62 M in organolithium and 0.22 M in bromide ion. The organolithium compound comprised 83% of the total base. The yield of phenyllithium was 0.65 mole (65%). Phenyllithium solutions prepared and stored in this manner could be kept at room temperature for as long as 3 months with no appreciable change in organolithium titer. Aliquots of this solution were transferred under nitrogen to the reaction-rate flask by means of a specially designed delivery pipet.

The n-butyl ether used as a solvent in the phenyllithium-initiated rates was purified according to the procedure of Coleman and Brooks,[15] distilled under purified nitrogen from about one-thirtieth its volume of a 1 M solution of methylmagnesium iodide in n-butyl ether (Arapahoe Chemical Co.), and stored under purified nitrogen over sodium metal and calcium hydride. n-Butyl ether purified in this manner is referred to as "purified n-butyl ether."

The "purified nitrogen" was prepared by passing nitrogen containing less than 8 p.p.m. of oxygen (Matheson Co.) through: (1) Fieser solution[16] to remove the oxygen, (2) saturated lead acetate solution to remove the hydrogen sulfide generated by the Fieser solution, (3) concentrated

(6) P. Fritsch, Ann., 279, 319 (1894).

(7) W. P. Buttenberg, ibid., 279, 324 (1894).

(8) H. Wiechell, ibid., 279, 337 (1894).

(9) (a) C. H. Coleman and R. D. Maxwell, J. Am. Chem. Soc., 56, 132 (1934); (b) C. H. Coleman, W. H. Holst and R. D. Maxwell, ibid., 58, 2310 (1936).

(10) (a) A. A. Bothner-By, ibid., 77, 3293 (1955); (b) J. G. Prichard and A. A. Bothner-By, Abstracts of Papers of the 135th Meeting of the American Chemical Society, Boston, Mass., April, 1959, p. 35-R.

(11) D. Y. Curtin, E. W. Flynn and R. F. Nystrom, J. Am. Chem. Soc., 80, 4599 (1958).

(12) (a) D. Y. Curtin, E. W. Flynn, R. F. Nystrom and W. H. Richardson, Chemistry & Industry, 1453 (1957); (b) D. Y. Curtin and E. W. Flynn, J. Am. Chem. Soc., 81, 4714 (1959); (c) D. Y. Curtin and W. H. Richardson, ibid., 81, 4719 (1959); (d) E. W. Flynn, Ph.D. Thesis, University of Illinois, 1956.

(13) S. J. Cristol and R. S. Bly, Jr., J. Am. Chem. Soc., 82, 142 (1960).

(14) T. W. J. Taylor and A. R. Murray, J. Chem. Soc., 2078 (1938).

(15) G. H. Coleman and J. W. Brooks, J. Am. Chem. Soc., 68, 1620 (1946).

(16) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1955, pp. 299–300.

sulfuric acid to remove the moisture, and (4) a tower of soda-lime to remove any sulfuric acid and carbon dioxide which might be present. The nitrogen used to blanket the phenyllithium-induced rate determinations was saturated with purified n-butyl ether by passing it through a gas washing bottle containing this solvent thermostated at the temperature of the reaction flask.

Standardizations and Analytical Procedures.—The method used for the standardization of the phenyllithium solution was developed by Helmreich.[2a] Two milliliters of inorganic-halide-free 1-bromo-2-phenylethene (Eastman P-283) was placed in a 200-ml. volumetric flask and 15 ml. of purified n-butyl ether was added. The flask was flushed with purified nitrogen and an aliquot of phenyllithium solution in purified n-butyl ether was added with the delivery pipet. The flask was swirled to mix the contents, stoppered, and allowed to stand at 20° for 1 hour. At the end of this time, 15 ml. of 1.5 M nitric acid was added, the flask was shaken vigorously, and enough 92.6 wt. % ethanol was added to dilute the contents to the mark. An aliquot of this solution was then titrated for halide ion by the modified Volhard procedure of Kolthoff and Sandell[17] using 0.03 M aqueous silver nitrate and 0.02 M potassium thiocyanate. The resulting halide-ion concentration, for purposes of identification, will be referred to as the "equivalent total halide."

The above procedure was repeated with a second 200-ml. volumetric flask containing 15 ml. of purified n-butyl ether but no 1-bromo-2-phenylethene. The resultant halide-ion contration will be termed "excess halide." An aliquot of this second solution also was titrated with standard 0.01 N sulfuric acid to a phenolphthalein end-point. The resulting base concentration will be referred to as "equivalent total base."

Since Helmreich[2a] has shown that 1 mole of bromide will be liberated for each 2 moles of organolithium compound consumed, the concentration of the solution can be calculated as follows: phenyllithium = 2(equivalent total halide − excess halide) and excess base = (equivalent total base − phenyllithium), where the expression "excess halide" denotes the amount of halide ion initially contained in the phenyllithium solution, and the term "excess base" denotes the base other than organolithium compound which was present in the solution. The phenyllithium solution was analyzed in this manner before the start of each rate determination.

Determination of Solvent Density.—The density of n-butyl ether at the various temperatures used in these rate measurements is given in Table I. These values were obtained by graphical interpolation of the data of Bingham and Spooner.[18]

TABLE I

THE DENSITY OF n-BUTYL ETHER

Temp., °C.	Density, g./ml.	Temp., °C.	Density, g./ml.
11.70	0.7743	43.73	0.7467
20.00	.7660	63.71	.7287
23.08	.7644	75.03	.7184
23.63	.7640	86.52	.7078
34.40	.7548		

Procedure for Rate Determinations and Treatment of Data.—These rates were run under purified nitrogen in a special rate flask designed so that aliquots of the thermostated reaction mixture could be removed at will without introducing air into the system. Using this apparatus, it was possible to carry out rate determinations above or below room temperature and to take up to 19 samples as close as 75 seconds apart. In an actual rate determination, samples were withdrawn throughout the course of the reaction and quenched by addition to 5 ml. of 1.5 M nitric acid solution. The initial time was taken when the phenyllithium solution was mixed in the rate flask with the solution of chlorodiphenylethene. The final time was taken when the aliquot of the reaction mixture was added to the nitric acid solution. The rates were followed by Volhard titra-

(17) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., rev. ed., 1949, p. 573.

(18) E. C. Bingham and L. W. Spooner, *J. Rheology*, **3**, 221 (1932).

tion of the total halide ion as described previously. A correction was made for the amount of bromide ion introduced with the phenyllithium solution.

The second-order rate constants were calculated from the best straight lines, drawn by inspection, through the points on a plot of log $[(1 - b\phi/a)/(1 - \phi)]$ vs. time where $a =$ initial phenyllithium concentration, $b =$ initial chlorodiphenylethene concentration, and ϕ is the fraction of chlorodiphenylethene reacted at time t. Values of the second-order rate constants obtained in this manner are given in Table II. Plots of typical kinetic runs are given in Figs. 1, 2 and 3.

TABLE II

RATES OF PHENYLLITHIUM-INDUCED DEHYDROCHLORINATION OF CHLORODIPHENYLETHENES

Compd.	Temp., °C.	[Compd.],[a] mole/l.	[C6H5-Li],[a] mole/l.	[Br−],[a,b] mole/l.	10^4 k [c]	10^4 k_{av} [c]
1-Chloro-*trans*-1,2-diphenyl-ethene	43.73	0.00556	0.0228	0.0086	4.34	4.12
		.00556	.0228	.0086	4.52	
		.00556	.0235	.0108	3.51	
	63.71	.00441	.0212	.0105	22.2	22.0
		.00441	.0213	.0106	21.7	
	75.03	.00364	.0171	.0088	62.8	48.0
		.00534	.0197	.0103	43.2	
		.00436	.0206	.0105	50.4	
		.00436	.0210	.0105	48.1	
		.00334	.0211	.0107	50.3	
		.00544	.0256	.0133	44.1	
	86.52	.00430	.0200	.0103	117	120
		.00430	.0203	.0103	122	
1-Chloro-*cis*-1,2-diphenylethene	23.08	.00336	.0163	.0062	29.0	29.0
		.00569	.0291	.0105	26.8	
	23.63	.00327	.0168	.0089	31.6	32.0
		.00327	.0170	.0088	32.4	
	34.40	.00335	.0107	.0041	86.7	67.6
		.00335	.0110	.0041	78.8	
		.00332	.0167	.0062	68.8	
		.00332	.0168	.0062	66.3	
		.00459	.0231	.0086	50.9	
		.00459	.0232	.0085	59.0	
		.00459	.0232	.0085	59.6	
	43.73	.00332	.0110	.0041	139	115
		.00329	.0165	.0063	116	
		.00329	.0166	.0062	114	
2-Chloro-1,1-diphenyl-ethene	11.70	.00390	.0146	.0060	109	96.4
		.00380	.0154	.0061	114	
		.00380	.0161	.0060	92.5	
		.00380	.0167	.0060	87.8	
		.00375	.0170	.0062	78.7	
	23.08	.00382	0134	.0053	218	228
		.00371	.0160	.0061	238	
	23.63	.00379	.0157	.0088	232	230
		.00379	.0161	.0087	227	
	34.40	.00337	.0104	.0041	467	437
		.00337	.0112	.0041	437	
		.00377	.0155	.0087	431	
		.00376	.0162	.0084	465	
		.00375	.0164	.0085	486	

[a] Given at the temperature at which the rates were determined. [b] "Excess halide" present as a contaminant in the phenyllithium solution. [c] In liters moles^{-1} sec.$^{-1}$.

These rates were followed to about 45–55% reaction in the case of the 1-chloro-*cis*-1,2-diphenylethene (I), 40–50% reaction in the case of the 1-chloro-*trans*-1,2-diphenylethene (II), and 55–65% reaction for the 2-chloro-1,1-diphenylethene (III).

From an examination of the data recorded in Table II, it is evident that an increase in the base and/or bromide-ion concentration causes some decrease in the second-order rate constants of the β-eliminations. No such effect is apparent in the α-elimination. Curtin and Flynn[12b] have reported that the presence of excess inorganic halide ion in the reaction mixture seems to have a marked inhibitory effect on the rates of related α-eliminations in similar systems. Helmreich was unable to demonstrate any effect upon the rate of reaction of *cis*- or *trans*-1-bromo-2-phenylethene with phenyllithium in n-butyl ether by added in-
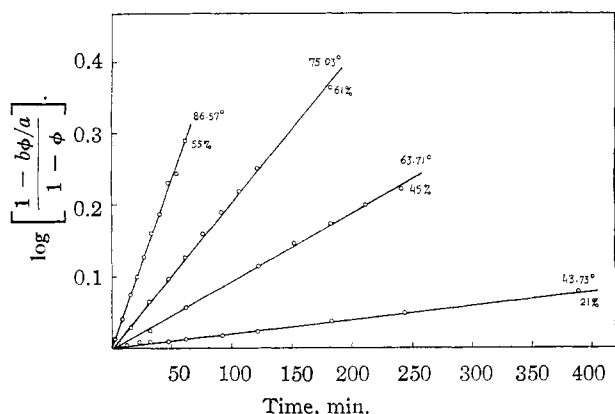
Fig. 1.—The rate of dehydrochlorination of 1-chloro-trans-1,2-diphenylethene with phenyllithium in n-butyl ether.
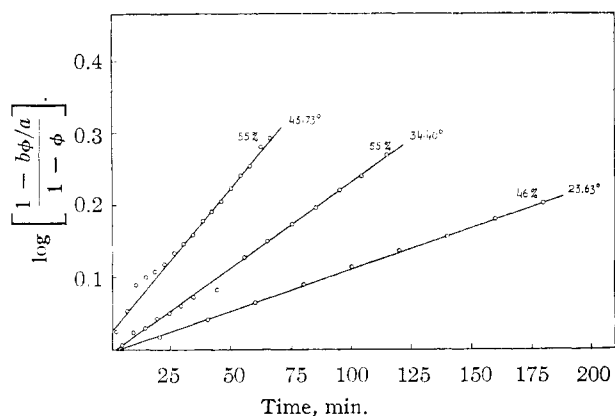

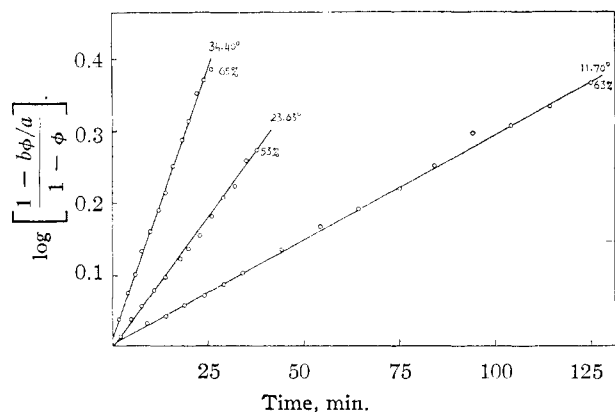Fig. 2.—The rate of dehydrochlorination of 1-chloro-cis-1,2-diphenylethene with phenyllithium in n-butyl ether.

Fig. 3.—The rate of dehydrochlorination of 2-chloro-1,1-diphenylethene with phenyllithium in n-butyl ether.

organic halide ion. Since we made no effort to vary independently the base and the bromide-ion concentration at the start of the reactions, we cannot say whether the effect which we have observed with the β-eliminations is more properly ascribed to a failure of these reactions, 8 and 9, to obey simple second-order kinetics, or to an unusual salt effect which may be connected in some manner with the known ability of phenyllithium to form addition compounds with lithium bromide in ether solution.[4a,b,19]

(19) G. Wittig, F. J. Meyer and G. Lange, Ann., 571, 167 (1951).
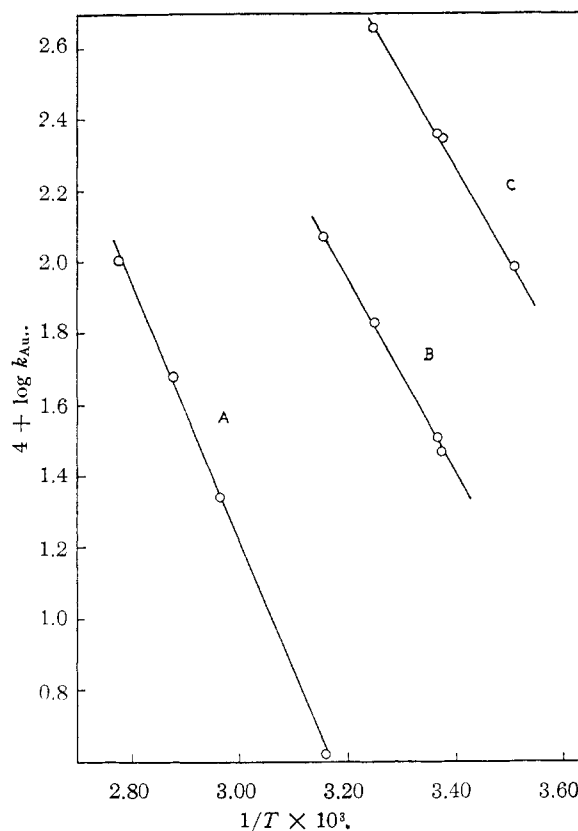

Fig. 4.—Plot for the calculation of the Arrhenius energies of activation for the dehydrochlorination of (A) 1-chloro-trans-1,2-diphenylethene, (B) 1-chloro-cis-1,2-diphenylethene and (C) 2-chloro-1,1-diphenylethene with phenyllithium in n-butyl ether.

Because of these observed variations of second-order rate constant with base and/or bromide-ion concentration, we have used for the calculation of the activation energies and entropies of the β eliminations average rate constants computed from runs at as nearly the same base and bromide-ion concentrations as possible (see Table II).

The Arrhenius activation energies were calculated in the usual manner from a plot of $1/T$ vs. log k_{av} (see Fig. 4). The entropies of activation were calculated from the Eyring equation[20] using the second-order rate constants at 50.00°, read from the appropriate Arrhenius plot. These quantities are listed in Table III. Included for comparison are the comparable quantities obtained from rates run on the same compounds with sodium hydroxide in 92.6 wt.% ethanol.[5]

TABLE III

ACTIVATION ENERGIES AND ENTROPIES FOR THE DEHYDRO-CHLORINATION OF CHLORODIPHENYLETHENES

Diphenylethene	$10^4 k$, l./mole/sec.	Ea, kcal./mole	ΔS*, e.u.
(A) Sodium hydroxide-induced dehydrochlorination[5]			
1-Chloro-trans-1,2-	9.04[a]	28.1	+1.0
1-Chloro-cis-1,2-	0.0435[a]	33.7	+5.6
2-Chloro-1,1-	0.00039[a]		
(B) Phenyllithium-induced dehydrochlorination			
1-Chloro-trans-1,2-	7.71[b]	18.5	−18
1-Chloro-cis-1,2-	175[b]	12.6	−30
2-Chloro-1,1-	1210[b]	12.2	−27

[a] Read from an Arrhenius plot at 97.00°.[5] [b] Read from Fig. 4 at 50°.

(20) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 199.

Determination of Reaction Products with Phenyllithium.
—The products of the reactions with phenyllithium in
n-butyl ether were determined by allowing phenyllithium to
react under purified nitrogen with the chlorodiphenylethene
in n-butyl ether. After an appropriate length of time, 12–
15 half-lives, the reactions were quenched in 1.5 M nitric
acid, extracted with ethyl ether and chromatographed on
alumina (Brockmann Activity II) using pentane as an eluent.
The resulting fractions were identified by mixed melting
point determinations with known compounds and by their
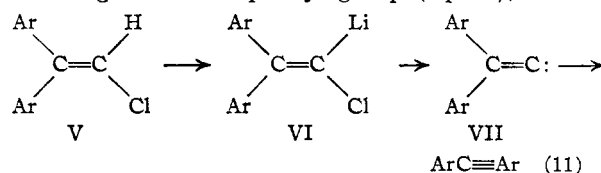infrared spectra.

The reaction products recovered from the treatment of
1-chloro-*trans*-1,2-diphenylethene (II) with phenyllithium
at 43° consisted of 79% tolan (IV) and 21% oily crystals
which were presumed from their infrared spectrum to be a
mixture of tolan and starting material. The 1-chloro-*cis*-
1,2-diphenylethene (I), when treated in the same manner
with phenyllithium in n-butyl ether at 23°, gave a mixture
composed of about 85% tolan and 15% starting material.
The infrared spectra showed no evidence of either *cis*- or
trans-stilbene in the products of either of these β-elimi-
nations. When 2-chloro-1,1-diphenylethene (III) was
treated in the same manner at 20°, 80% of the theoretical
amount of tolan was recovered together with a considerable
quantity of biphenyl and some phenol.[21] No chlorobenzene
or 1,1-diphenylethene (VIII) was found in the products of
the reaction.

Discussion

Any mechanisms which may be considered for
the elimination reactions of the isomeric diphenyl-
chloroethylenes must account for these various
facts. With the weaker base, sodium hydroxide,
trans-β-elimination (in a particularly poor situa-
tion[5]) is 23,000 times faster than α elimination,
with *cis*-β-elimination lying in between. With
phenyllithium as base the order is exactly reversed,
α-elimination being 7 times as rapid as *cis*-β,
and 160 times as rapid as *trans*-β-elimination.[23]

In the earlier work[2] with isomers of β-bromo-
styrene and phenyllithium, we were struck with
the similarity in reactivity in both *cis* and *trans*
elimination (see above) and suggested that an α-
elimination process for both isomers would ac-
commodate the data. This concept would, of
course, predict the order of reactivity which we
have now observed for the isomeric diphenyl-
chloroethylenes, although the existence of this
process for the bromostyrenes now appears less
attractive.[11]

Several possible routes, with differing stereo-
chemical implications, may be considered for the
elimination processes in the three cases reported
in this paper. For the α-elimination, which
proceeds with over-all loss of hydrogen chloride
and migration of a phenyl group (eq. 10), certain

$$ArC\equiv Ar \quad (11)$$

possibilities offer themselves. If the α-elimination
were complete before rearrangement (eq. 11),
an unsaturated carbene species (VII) would in-
tervene. The existence of such an intermediate
finds support in recent work,[24,25] where evidence
for carbenes in the reaction of certain saturated
alkyl halides with very strong bases is adduced.
The question of the stereochemistry of unsaturated
carbenes is important, as the mechanism must
accommodate the preferred migration of the aryl
group *cis* to the hydrogen atom in V.[10–12] If the
carbene carbon atom maintained its sp^2-character
(with one such hybrid orbital occupied by an elec-
tron pair and the other unoccupied) for its singlet
state, the stereospecificity of rearrangement could
be understood. If, however, rehybridization of
the carbene carbon atom occurred upon formation,
in such a way as to utilize an sp-orbital to form
the σ-bond, an sp-orbital to hold the unshared
electron pair and the two remaining p-orbitals
(one to form the π-bond and the other to remain
unoccupied), no preferred stereochemistry would
be observed.[26]

A mechanism in which a carbanion (or the equiv-
alent organolithium reagent VI) is involved must
also be considered. It is clear from recent work[27,28]
that unsaturated organolithium compounds have
considerable configurational stability, and also
that vinyl carbanions appear to have a large barrier
to interconversion.[29] The mechanism thus re-
sulting is indicated in eq. 12. One notes that this
mechanism is formally analogous to that of the

$$V \rightarrow \begin{bmatrix} \text{VIII} \end{bmatrix}^- \quad \text{or} \quad VI \rightarrow ArC\equiv C-Ar + Cl^- \quad (12)$$
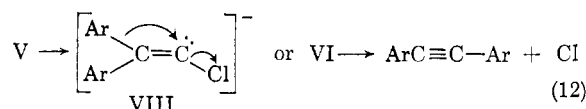
Beckmann rearrangement, where evidence for
migration of an electron pair attached to an alkyl
or aryl group concerted with loss of the anionoid
species is formidable.[30] This mechanism is suit-
able so long as the life-time of the intermediate
carbanion in its reaction to give tolan is short com-
pared with that of *cis–trans* interconversion.[12]
It is of interest to note that the direction of electron
flow in process 12 is opposite to that generally
assumed in carbanionoid rearrangements,[31] but

(21) Biphenyl is known to be formed as a by-product in the syn-
thesis of phenyllithium from bromobenzene and lithium metal.[22]
The phenol may originate from the hydrolysis of the lithium phenoxide
produced by the reaction of oxygen with phenyllithium. The batches
of phenyllithium used in the rate measurements were prepared under
purified nitrogen.

(22) H. A. Pacevitz and H. Gilman, *J. Am. Chem. Soc.*, **61**, 1603
(1939).

(23) For a summary of alkali-initiated bimolecular dehydrohalo-
genations, see D. J. Cram, in Newman's "Steric Effects in Organic
Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, pp.
305–348.

(24) W. Kirmse and W. von E. Doering, *Tetrahedron*, **11**, 266
(1960).

(25) L. Friedman and J. G. Berger, *J. Am. Chem. Soc.*, **83**, 492, 500
(1961).

(26) It would appear that the latter hybridization would be favored,
as the shortening of the σ-bond resulting from sp^2-sp overlap rather
than sp^2-sp^2 overlap would lead to more stable σ- and π-bonds.

(27) (a) D. Y. Curtin and E. E. Harris, *J. Am. Chem. Soc.*, **73**,
2716, 4519 (1951); (b) D. Y. Curtin, H. W. Johnson, Jr., and E. G.
Steiner, *ibid.*, **77**, 4566 (1955); (c) D. Y. Curtin and J. W. Crump,
ibid., **80**, 1922 (1958); (d) D. Y. Curtin and W. J. Koehl, Jr., *Chemis-
try & Industry*, 262 (1960); Abstracts of Papers presented before the
138th Meeting of the American Chemical Society, New York, N. Y.,
September, 1960, p. 53-P.

(28) (a) A. N. Nesmeyanov, A. E. Borisov and N. A. Volkenau,
Izvest. Akad. Nauk S.S.S.R., 992 (1954) [*C. A.*, **49**, 6892 (1955)];
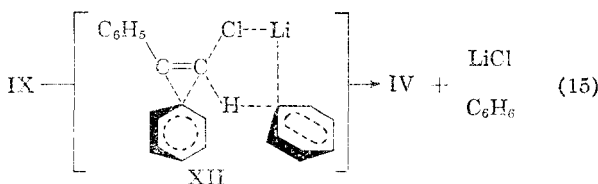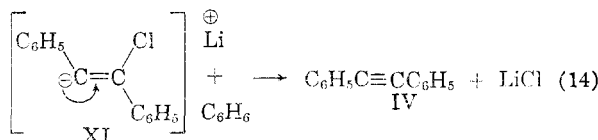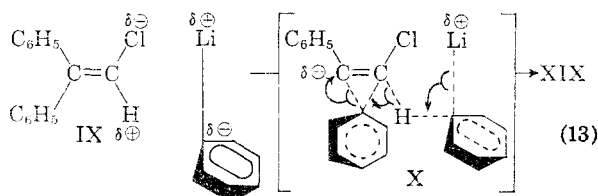(b) A. N. Nesmeyanov and A. E. Borisov, *Tetrahedron*, **1**, 158 (1957).

(29) S. I. Miller and W. G. Lee, *J. Am. Chem. Soc.*, **81**, 6313 (1959).

(30) For appropriate references, see L. G. Donaruma and W. Z.
Heldt, *Org. Reactions*, **11**, 1 (1960).

(31) H. E. Zimmerman and A. Zweig, Abstracts of Papers of the
137th Meeting of the American Chemical Society, Cleveland, Ohio,
April, 1960, p. 17-O.

this is necessary to keep the analogy to the isosteric Beckmann rearrangement. Bothner-By has discussed this mechanism in considerable detail.[10a]

Certain mechanisms in which the migration of the aryl group is concerted with the removal of the proton should also be considered. The system represented as IX in eq. 13, which in eq. 12 is assumed to lead to the carbanion VIII or VI, also may be assumed as in 13, to lead to a carbanionoid rearrangement concerted with the carbon–hydrogen bond breaking. The processes described in eq. 13 and 14 compared with that represented by 15 differ only in the concertedness of chloride-ion loss. We can conceive of two possibilities, both of which would start with associated dipoles IX.

$$\text{(13)}$$

$$C_6H_5C\equiv CC_6H_5 + LiCl \quad (14)$$

$$IX \longrightarrow \cdots \longrightarrow IV + \begin{array}{c} LiCl \\ C_6H_6 \end{array} \quad (15)$$

The implications of the various mechanisms regarding the effects of structure upon rearrangement and reactivity are amenable to testing, and work in this area is planned.

In the case of the β-eliminations, carbene intermediates are not possible, and one needs to consider only lithium–hydrogen exchange (or carbanion formation), followed by or concerted with chloride-ion loss (we found no evidence for lithium–halogen exchange in these systems). By analogy to the carbanion (eq. 12), the semi-cyclic (13–14) and the cyclic (15) processes suggested for the α-elimination, the following two mechanisms can be written for the cis-β-dehydrochlorination. Like the mechanisms for α-elimination, each is initiated by coordination of the positive end of the phenyllithium dipole with the chlorine atom of the vinyl halide. A cyclic transition state such as XVI is similar to that postulated by Letsinger and Bobko[32] to explain the more rapid cis elimination of the ele-

(32) R. L. Letsinger and E. Bobko, J. Am. Chem. Soc., 75, 2649 (1953).

$$\text{(16)}$$

$$C_6H_5\equiv CC_6H_5 + LiCl \quad (17)$$

$$\text{(18)}$$
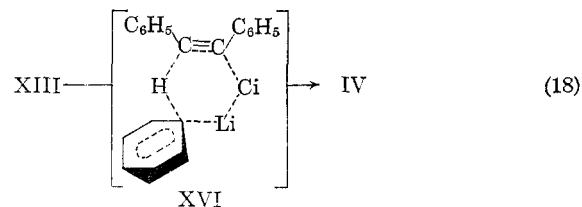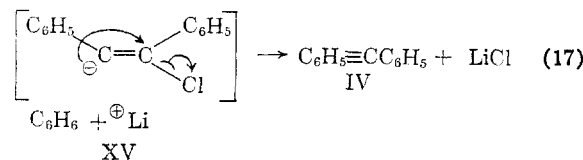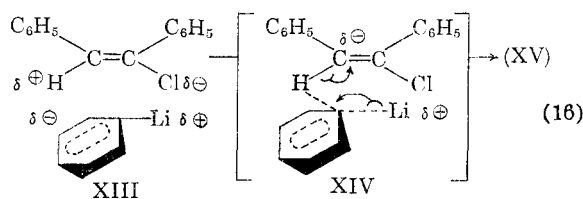
ments of methanol when cis- and trans-1-methoxy-2-phenylcyclohexane are heated under reflux with n-butyllithium in a mixture of pentane and ethyl ether.

An examination of our rate data, Table III, discloses that both the cis-β- and the α-eliminations proceed with essentially identical activation energies, that the entropies of activation for both of these reactions are quite unfavorable, and that the entropy of activation is slightly more unfavorable for the cis elimination than for the α-elimination. This similarity in the activation energies and entropies for these two eliminations suggests that their mechanistic courses may also be similar, although this is by no means certain. The highly unfavorable entropy is easily rationalized in all of the proposed mechanisms by the constraint involved in forming the five- or six-membered rings, associated with the complexing of the lithium atom by the chlorine atom and with the removal of the proton by the anionoid phenyl. It will be of interest to compare kinetic data for these systems with phenyllithium with similar data with other strong (but dissociated) bases, when such data are available.

The rate data further indicate that the trans-β-elimination requires a considerably higher activation energy than either the cis-β- or the α-elimination, but that the entropy of activation is not as unfavorable as in these latter two processes. The geometry of the trans system rules out the possibility of a cyclic transition state, but the question of whether the process involves a carbanion (or vinyllithium) intermediate or is concerted remains.